



# Tailoring the Mo-N/Mo-O configuration in MoO<sub>2</sub>/Mo<sub>2</sub>N heterostructure for ampere-level current density hydrogen production

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## ABSTRACT

Mo-based electrocatalysts have garnered significant attention for their promising hydrogen evolution reaction (HER) efficiency, however, the strong adsorption of hydrogen poses a challenge to speedy gaseous hydrogen release. In this respect, regulating the coordination of Mo atoms is an efficient strategy to optimize the electronic configuration and accelerate the HER kinetics. Herein, MoO<sub>2</sub>/Mo<sub>2</sub>N heterostructures are prepared by a programmed *in situ* nitridation process. The precisely controlled Mo-N/Mo-O configuration in MoO<sub>2</sub>/Mo<sub>2</sub>N heterostructure weakens hydrogen adsorption on the Mo sites leading to HER with an ampere-level current density. The electrocatalyst delivers 1 A cm<sup>-2</sup> at an overpotential of 335 mV in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Furthermore, the electrocatalyst has excellent stability by maintaining a current density of 1 A cm<sup>-2</sup> for 180 hours with a remarkable Faradaic efficiency of 99.8%. The results reveal a novel strategy to precisely modulate the electronic configurations of low-cost transition metal-based electrocatalysts boding well for industrial-scale hydrogen production.

## 1. Introduction

Owing to the renewable and environment-friendly properties, hydrogen has garnered broad attention as a promising alternative to fossil fuels [1–4]. In particular, hydrogen production by the hydrogen evolution reaction (HER) in electrochemical water splitting can be powered by sustainable energy sources to accomplish zero carbon emission [5,6]. However, efficient electrocatalysts are required for large current density HER in commercial electrochemical water splitting [7–11]. Wang et al. [7] have reported RuCo@Ru<sub>5</sub>CoSA-NMC with a low overpotential of 255 mV for a current density of 1 A cm<sup>-2</sup> and Zhang et al. [12] have constructed a robust self-supporting electrode of Ru-Ni(OH)<sub>2</sub> with excellent HER activity such as a current density of 2000 mA cm<sup>-2</sup> at a small overpotential of 400 mV. Precious metals electrocatalysts are normally required to produce a large current density in HER, but their high cost and natural scarcity hinder wide commercial

implementation, especially HER with ampere-level current densities. Hence, it is imperative to develop cost-effective and highly active non-noble metal-based electrocatalysts for industrial HER.

Mo-based compounds are promising HER electrocatalysts due to the abundant natural reserves and tunable configurations of the active sites [13,14]. In particular, molybdenum nitride (Mo<sub>2</sub>N) is extensively studied for HER due to its distinctive electronic structure, high electrical conductivity, and mechanical stability [15,16]. However, the HER activity of Mo<sub>2</sub>N is limited by the sluggish desorption of hydrogen because of the strong Mo-H bonding [17,18]. In this respect, regulating the electronic structure of the active sites can optimize the hydrogen adsorption characteristics and enhance the HER kinetics. Zhou et al. [19] have reported that the electronic interactions between the two phases in a heterostructure can be exploited to modify the hydrogen adsorption properties at the heterointerface to improve the HER efficiency. Fu et al. [20] have designed CoO-Mo<sub>2</sub>N hollow heterojunctions

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for effective HER based on the combined virtues of the hollow structure and heterojunctions. The CoO in CoO-Mo<sub>2</sub>N facilitates the dissociation of water and the catalyst presents outstanding HER performance with an overpotential of 65 mV to afford the current density of 10 mA cm<sup>-2</sup> in 1 M KOH. Previous works proved that combining the molybdenum nitride with oxides is beneficial to the optimized hydrogen adsorption properties and accelerated HER [21–23]. Considering that molybdenum dioxide (MoO<sub>2</sub>) has low electrical resistivity and high stability, which has attracted much attention [24,25]. Constructing a heterostructure consisting of Mo<sub>2</sub>N and MoO<sub>2</sub> with tailorable content and configuration would deliver favorable HER capability, which has seldom been reported and is challenging.

Herein, a coordination modulation strategy is designed and implemented to regulate the Mo-O/Mo-N configuration in the MoO<sub>2</sub>/Mo<sub>2</sub>N heterostructure obtained by *in situ* phase separation from MoO<sub>3</sub> nanowires. The amounts of Mo-O and Mo-N can be controlled precisely by a programmed nitridation process to produce superior HER properties with ampere-level current densities. For example, a high current density of 1 A cm<sup>-2</sup> can be achieved at an overpotential of 335 mV in 0.5 M H<sub>2</sub>SO<sub>4</sub> together with a Tafel slope of 88 mV dec<sup>-1</sup>. In addition, the electrocatalyst works stably for 180 hours at a current density of 1 A cm<sup>-2</sup>. Density-functional theory (DFT) calculations reveal that the MoO<sub>2</sub>/Mo<sub>2</sub>N heterostructure weakens H\* absorption at the hetero-interface, especially at Mo atoms of the Mo<sub>2</sub>N phase, resulting in accelerated release of hydrogen from the active sites. The results provide insights into the modulation of active sites and the strategy has large potential in large current-density commercial hydrogen production.

## 2. Experimental details

### 2.1. Materials preparation

#### 2.1.1. Synthesis of the MoO<sub>3</sub>/CC precursor

Ammonium molybdate ((NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>) (0.75 g) was dissolved in 10 mL of deionized water (DW) and heated to 70 °C for 30 min. Concentrated nitric acid (HNO<sub>3</sub>) (40 mL) was added quickly to the solution under stirring and a piece of clean carbon cloth (CC) (2 × 3 cm<sup>2</sup>) was immersed in the solution for 30 min. Afterwards, the CC was washed with DW several times to remove impurities. The product was denoted as MoO<sub>3</sub>/CC.

#### 2.1.2. Synthesis of the MoO<sub>2</sub>/CC, MoON-x/CC, and Mo<sub>2</sub>N/CC electrocatalysts

The MoO<sub>3</sub>/CC precursor was annealed at 550, 600, and 650 °C for 2 h using a heating rate of 10 °C min<sup>-1</sup> in a tube furnace under ammonia. The products were designated as MoON-1, MoON-2, and MoON-3, respectively. The pure Mo<sub>2</sub>N/CC was synthesized by annealing the MoO<sub>3</sub>/CC precursor at 700 °C for 2 h in NH<sub>3</sub> at a heating rate of 10 °C min<sup>-1</sup>. The pure MoO<sub>2</sub>/CC was prepared by annealing the MoO<sub>3</sub>/CC precursor at 600 °C in N<sub>2</sub> for 2 h at a heating rate of 10 °C min<sup>-1</sup>.

### 2.2. Materials characterization

The morphology of the samples was examined by scanning electron microscopy (FE-SEM, TESCAN MIRA4) and transmission electron microscopy (TEM, FEIF200) coupled with energy-dispersive X-ray spectroscopy (EDS). The composition and crystal structure were determined by high-resolution TEM (HR-TEM), and X-ray diffraction (XRD, LabX XRD-6100, Shimadzu) with a Cu K<sub>α</sub> source. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Thermo Fisher) using monochromatic Al K<sub>α</sub> X-ray was conducted to determine the chemical state of the samples.

### 2.3. Electrochemical measurements

The electrochemical measurements were carried out using a three-

electrode configuration on the CHI 660E electrochemical workstation (Shanghai CH Instrument, China). The saturated calomel electrode (SCE) and graphite rod served as the reference electrode and counter electrode, respectively, and the electrocatalyst-modified CC was the working electrode. All the potentials were referenced to the reversible hydrogen electrode (RHE) according to Nernst equation  $E_{\text{RHE}} = E_{\text{SCE}} + 0.242 + 0.059 \times \text{pH}$ , where the pH of 0.5 M H<sub>2</sub>SO<sub>4</sub> was measured to be 0.56 by a pH meter (FE28, Mettler Toledo). Linear sweep voltammetry (LSV) was conducted at a scanning rate of 10 mV s<sup>-1</sup> with *iR*-compensation. The Tafel slope was calculated according to the formula  $\eta = a + b \log(j)$  ( $\eta$ , overpotential;  $j$ , current density;  $a$ , constant;  $b$ , Tafel slope). Electrochemical impedance spectroscopy (EIS) was carried out at the initial potential of -0.48 V vs. SCE in the frequency range of 100 kHz ~ 0.01 Hz with an amplitude of 5 mV. The electrochemically active surface area (ECSA) was determined by cyclic voltammetry (CV) at scanning rates of 15 ~ 40 mV s<sup>-1</sup> in the potential window between -0.05 and 0.05 V vs. SCE. The stability was determined at a constant current density of 1 A cm<sup>-2</sup> and the amount of H<sub>2</sub> and O<sub>2</sub> produced was determined by the water displacement method.

### 2.4. Density-functional theory calculations

The DFT calculation was performed using the slab model with a vacuum space of 15 Å along the *z*-direction [26]. The exchange-correlation function under the generalized gradient approximation within the Perdew-Burke-Ernzerhof function was implemented. The Brillouin zone was sampled with 1 × 1 × 1 *k*-point mesh in all of the models. The convergence tolerances of the optimal configuration for the energy, force, and maximum displacement were 1.0 × 10<sup>-5</sup> Ha, 0.002 Ha Å<sup>-1</sup>, and 0.005 Å, respectively.

The Gibbs free energy for hydrogen adsorption ( $\Delta G_{\text{H}^*}$ ) was calculated as follows:

$$\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + \Delta E_{\text{ZPE}} - T\Delta S \quad (1)$$

$$\Delta E_{\text{H}^*} = E_{(\text{slab}+\text{H}^*)} - E_{(\text{slab})} - \frac{1}{2}E_{\text{H}_2} \quad (2)$$

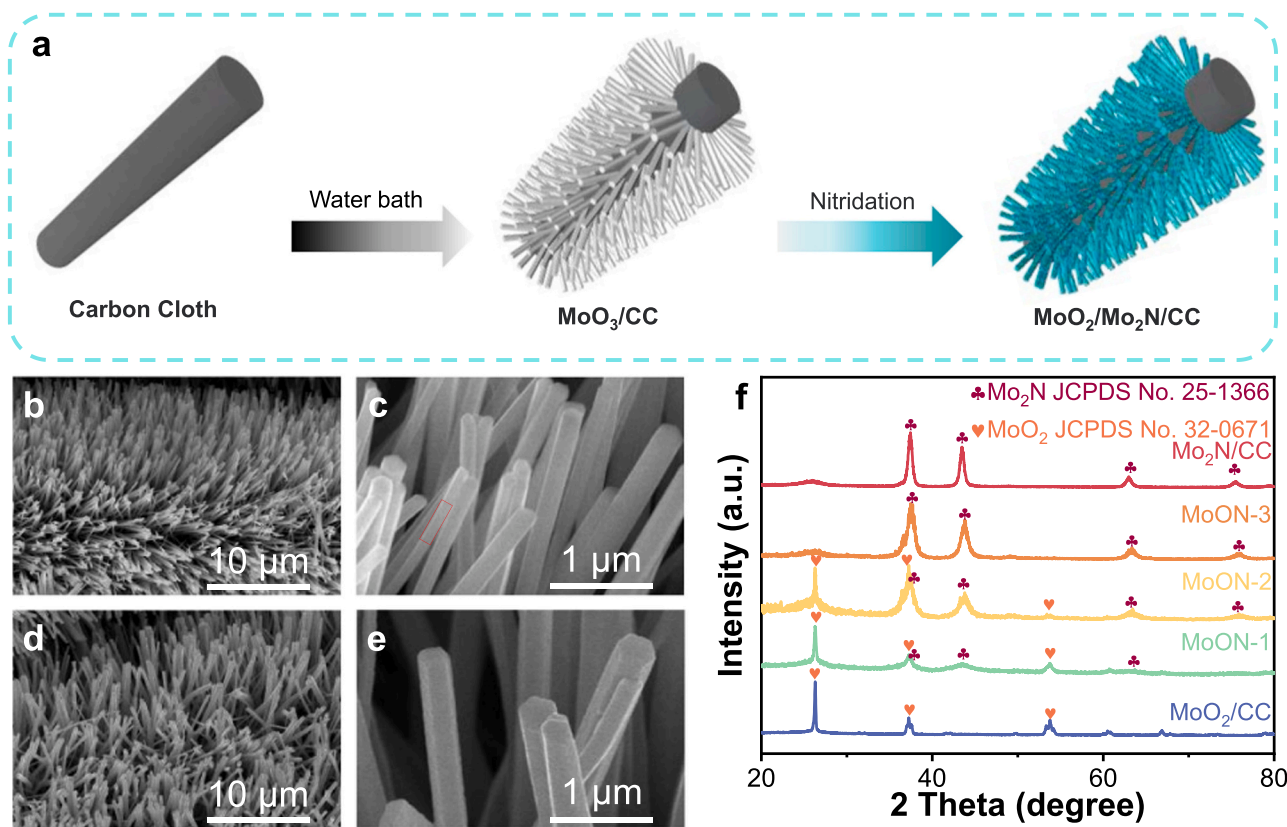
where  $\Delta E_{\text{ZPE}}$  stands for the change in the zero-point energy and  $\Delta S$  is the entropy. Here, we used the value of 0.24 eV for  $\Delta E_{\text{ZPE}} - T\Delta S$  according to Nørskov et al. [27].

## 3. Results and discussion

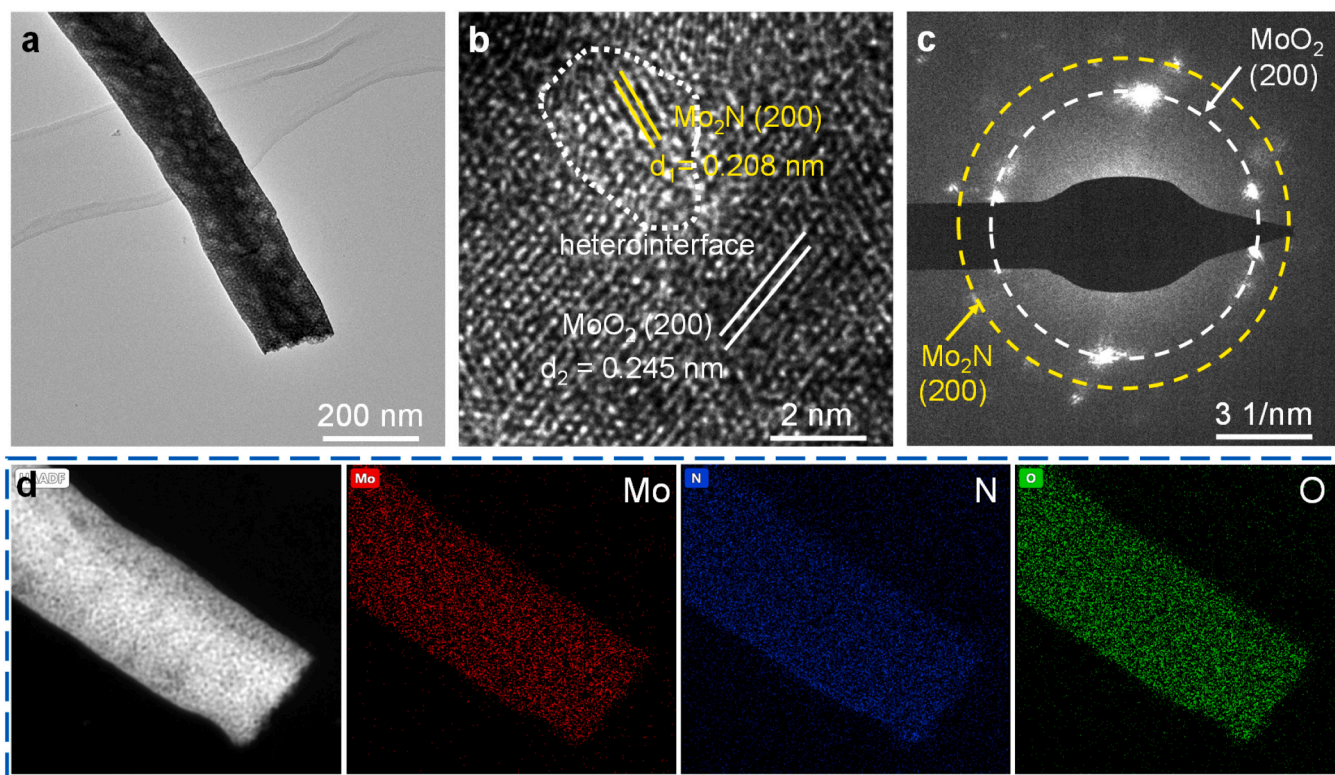
### 3.1. Morphology and composition of the electrocatalysts

Fig. 1a illustrates schematically the synthesis of the MoON electrocatalysts. The MoO<sub>3</sub> nanowire arrays are grown on the CC by a solution method in a hot bath with ammonium molybdate and nitric acid as the precursors. MoO<sub>3</sub> is then converted gradually into nitride by a programmed thermal treatment in an ammonia atmosphere. As a result, final products with different nitride concentrations are obtained. The tunable composition of Mo-O and Mo-N and subsequent interactions between these two phases modulate the electronic configurations of the Mo sites to enhance the electrocatalytic activity.

The FE-SEM images of MoO<sub>3</sub>/CC in Fig. 1b–c reveal that the nanowire arrays (120–180 nm in diameter) cover the carbon fibers. After the thermal treatment in ammonia at 550 ~ 700 °C, no obvious morphological change can be observed from Figs. S1–2 and 1d–e. The diameter of the nanowires is 150–250 nm. After the thermal treatment of MoO<sub>3</sub> in N<sub>2</sub> at 600 °C (MoO<sub>2</sub>/CC), the nanowire arrays on CC can also be observed in Fig. S3. XRD is performed to identify the phase and composition of the products. The diffraction peaks of the product obtained by the solution method can be indexed to MoO<sub>3</sub> (JCPDS card No. 21-0569), as shown in Fig. S4. After the thermal treatment in ammonia at 550 °C, the diffraction peaks at 37.4°, 43.5°, and 63.1° can be ascribed to Mo<sub>2</sub>N (JCPDS card No. 25-1366), whereas those at 26.0°,



**Fig. 1.** (a) Schematic showing the fabrication of the MoON electrocatalysts; SEM images of (b-c) MoO<sub>3</sub> and (d-e) MoON-2; (f) XRD patterns of MoO<sub>2</sub>/CC, MoON-1, MoON-2, MoON-3, and Mo<sub>2</sub>N/CC.



**Fig. 2.** (a) TEM image, (b) HR-TEM image with a dotted line showing the mismatch of the crystal planes, (c) SAED pattern, and (d) Elemental maps of Mo, N, and O in MoON-2.



37.0°, and 53.5° correspond to MoO<sub>2</sub> (JCPDS card No. 32–0671), suggesting that the product is a composite of Mo<sub>2</sub>N and MoO<sub>2</sub>, as indicated in Fig. 1f. By increasing the treatment temperature gradually from 550° to 700°C, the diffraction peaks from Mo<sub>2</sub>N are enhanced, but those from MoO<sub>2</sub> weaken. When the temperature is 650 °C, only Mo<sub>2</sub>N can be observed from Fig. 1f (red line), implying that MoO<sub>3</sub> has been converted into Mo<sub>2</sub>N by the programmed thermal treatment in ammonia. It is noted that in this technique, the ratio of Mo-based oxide and nitride can be controlled. In addition, by annealing the MoO<sub>3</sub>/CC at 600 °C for 2 h under N<sub>2</sub>, the pure phase of MoO<sub>2</sub> (JCPDS card No. 32–0671) can be produced, as shown in Fig. 1f (blue line).

The TEM image in Fig. 2a reveals the nanowire morphology of MoON produced by the solution method and the following thermal treatment in ammonia, which is similar to the SEM image. The nanowire is 170 nm in diameter. The HR-TEM image in Fig. 2b shows lattice fringes of 0.245 and 0.208 nm arising from MoO<sub>2</sub> (200) (JCPDS card No. 32–0671) plane and Mo<sub>2</sub>N (200) (JCPDS card No. 25–1366) plane, respectively. The mismatch of Mo<sub>2</sub>N and MoO<sub>2</sub> planes can be observed, as labelled in Fig. 2b, indicating the generation of heterointerface during the *in-situ* phase separation protocol, consistent well with the previous works [28, 29]. There will be atomic interaction at the heterointerface to optimize the electronic structure of the surface sites for facilitated electrocatalysis [30–32]. Fig. 2c presents the selected area electron diffraction (SAED) image of MoON-2. The diffraction rings can be assigned to MoO<sub>2</sub> and Mo<sub>2</sub>N matching the XRD and HR-TEM results. The EDS elemental maps of Mo, O, and N in Fig. 2d indicate homogeneous distributions of these elements.

The composition and chemical state of the electrocatalysts are determined by XPS. The survey spectra in Fig. 3a–b reveal the presence of Mo, O, and N elements in the samples thermally treated in ammonia. The high-resolution XPS Mo-3d spectra in Fig. 3c show two peaks at 236.1 and 232.8 eV stemming from Mo<sup>6+</sup>-O from slightly surface oxidation [33]. The peaks at 230.0 and 233.1 eV correspond to the Mo-3d<sub>5/2</sub> and Mo-3d<sub>3/2</sub> of Mo<sup>4+</sup>-O species in MoO<sub>2</sub> [28], and the other two peaks at 229.4 and 232.6 eV are associated with Mo-3d<sub>5/2</sub> and Mo-3d<sub>3/2</sub> of Mo-N in Mo<sub>2</sub>N [34,35]. The high-resolution XPS N-1s spectrum (Fig. S5) of MoON-2 shows the N-Mo bond at 398.1 eV and Mo-3p at 395.4 eV [36,37].

To determine the surface composition of the electrocatalysts, the amounts of Mo-O and Mo-N species are calculated based on the integrated areas in the fitted Mo-3d spectra. Fig. 3d shows that with the increasing treatment temperature in ammonia, the concentration of

Mo<sup>4+</sup>-O species decreases from 69% in MoON-1–30% in MoON-3. At the same time, the concentration of Mo-N increases from 11% in MoON-1–50% in MoON-3. The signal of Mo<sup>4+</sup>-O disappears when the temperature is increased to 700 °C, suggesting that the Mo-O species have been converted completely into Mo-N. The results also demonstrate that the amounts of Mo-O and Mo-N species can be modulated precisely by the programmed thermal treatment in ammonia. The *in situ* generated and precisely controlled Mo-N species interact strongly with the Mo-O host at the heterointerface. Hence, a well-designed Mo-O/Mo-N configuration at the heterointerface is expected to optimize hydrogen adsorption in HER for enhanced electrocatalytic efficiency.

### 3.2. Electrochemical properties

All the potentials were *iR* corrected unless otherwise specified to evaluate the intrinsically catalytic capability of the as-prepared electrocatalysts for HER. Fig. 4a shows the LSV curves of the Mo-based electrocatalysts in comparison with the bare CC and commercial Pt/C (20%) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. MoON-2 requires an overpotential of 300 mV for a current density of 500 mA cm<sup>-2</sup>, which is much smaller than those of MoON-1 (470 mV), MoON-3 (418 mV), Mo<sub>2</sub>N (517 mV), MoO<sub>2</sub> (640 mV), MoO<sub>3</sub> (853 mV), and commercial Pt/C (492 mV). Notably, the current density of MoON-2 electrocatalyst can reach 1 A cm<sup>-2</sup> at an overpotential of a mere 335 mV, which is distinctly smaller than that of the others. The LSV curves without *iR* compensation in Fig. S6 indicate the promising practical application of the MoON electrocatalyst. The Tafel slopes are obtained by fitting the linear regions of the Tafel plots. The Tafel slope of MoON-2 is 88 mV dec<sup>-1</sup>, which is smaller than those of MoON-1 (134 mV dec<sup>-1</sup>), MoON-3 (101 mV dec<sup>-1</sup>), MoO<sub>2</sub> (153 mV dec<sup>-1</sup>), MoO<sub>3</sub> (245 mV dec<sup>-1</sup>), Mo<sub>2</sub>N (110 mV dec<sup>-1</sup>), CC (287 mV dec<sup>-1</sup>) and close to that of commercial Pt/C (65 mV dec<sup>-1</sup>), as indicated in Fig. 4b. The Tafel slope of MoON-2 suggests the Volmer-Heyrovsky mechanism and electrochemical desorption of hydrogen is the rate-determining step [38]. The smaller overpotential and Tafel slope suggest higher electrocatalytic activity and faster kinetics for MoON-2. Moreover, Fig. 4c shows that MoON-2 has a smaller charge transfer resistance (*R*<sub>ct</sub>) of 8.5 Ω compared to MoON-1, MoON-3, Mo<sub>2</sub>N, MoO<sub>2</sub>, and commercial Pt/C thereby confirming the fast HER kinetics, which is promising for industrial-scale application.

The HER activity depends on the ECSA, which can be expressed by the electrochemical double-layer capacitance (*C*<sub>dl</sub>) in the non-Faradic regions based on the cyclic voltammetry curves [39], as shown in

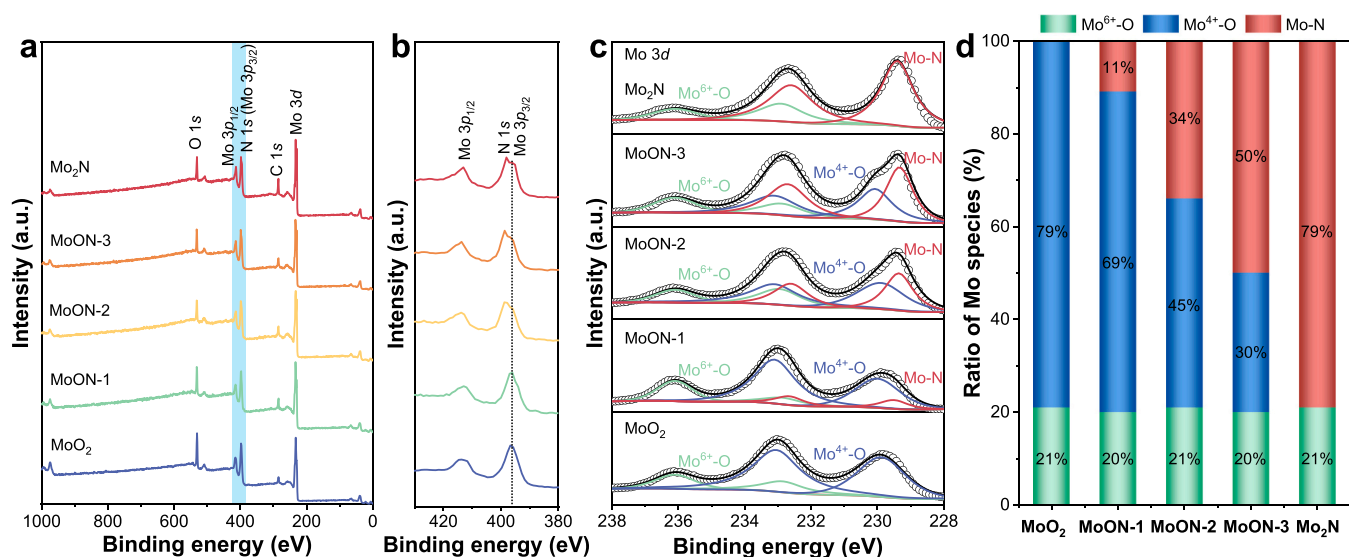
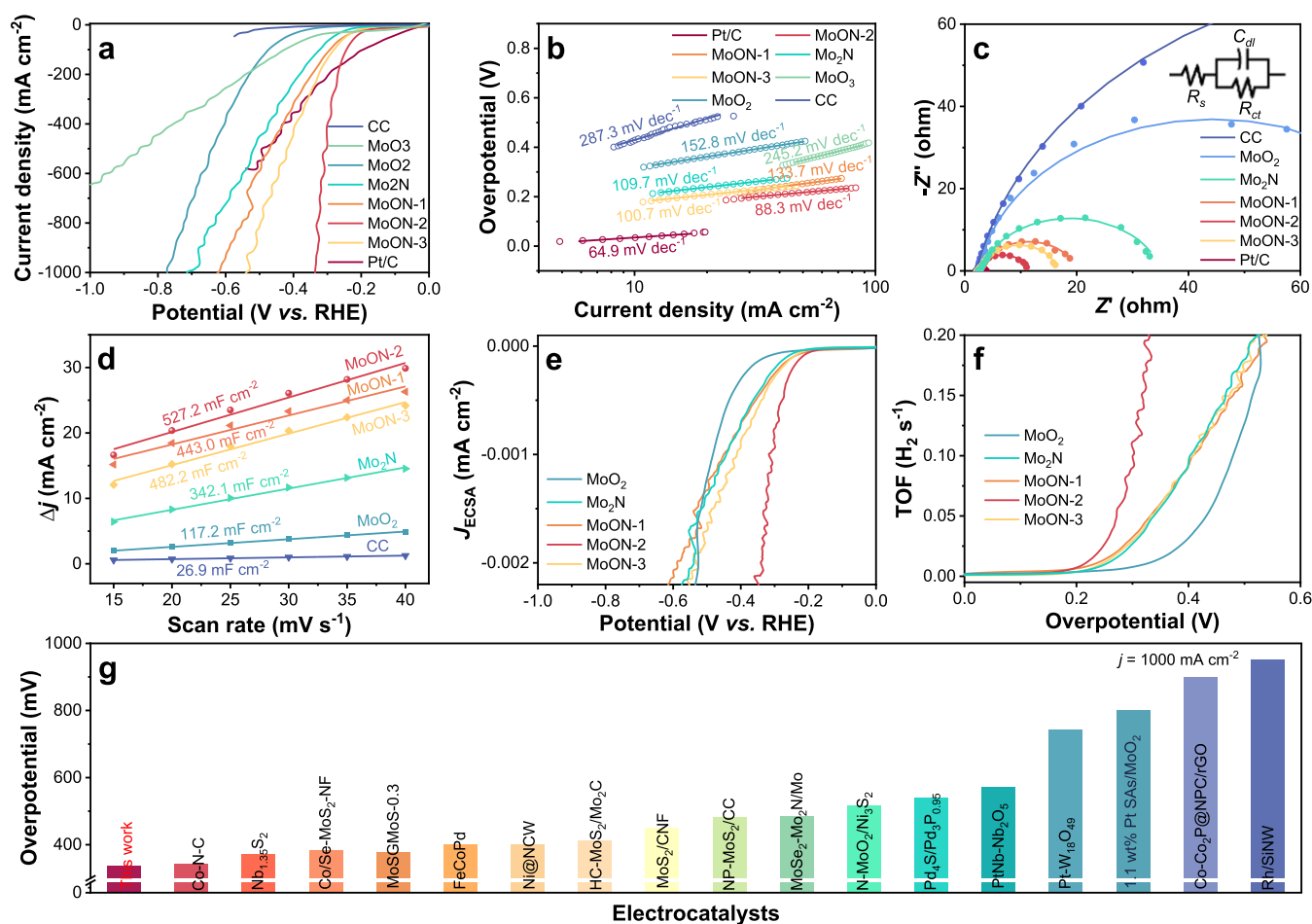


Fig. 3. XPS survey spectra of the electrocatalysts in the binding energy range of (a) 0 ~ 1000 eV and (b) 380 ~ 430 eV; (c) High-resolution XPS Mo-3d spectra; (d) Ratios of Mo species in MoO<sub>2</sub>, MoON-1, MoON-2, MoON-3, and Mo<sub>2</sub>N.



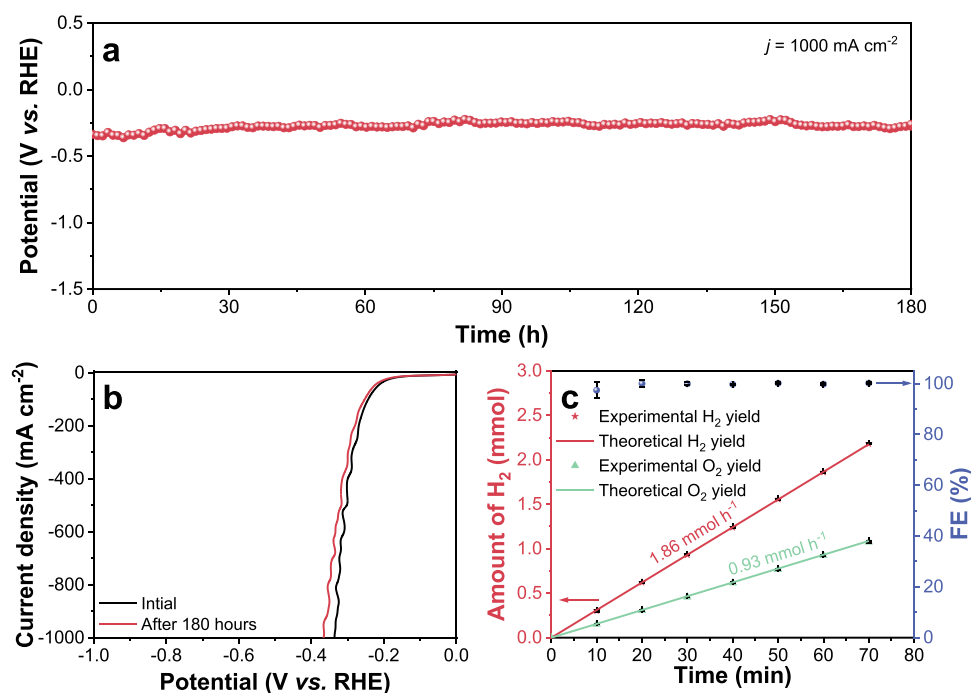
**Fig. 4.** HER properties of MoO<sub>2</sub>, MoON-1, MoON-2, MoON-3, and Mo<sub>2</sub>N in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (a) LSV curves; (b) Tafel plots; (c) EIS; (d) ECSA; (e) LSV based on the ECSA; (f) TOF; (g) Comparison of the overpotentials of the electrocatalyst at 1000 mA cm<sup>-2</sup> with those of other state-of-the-art electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

**Fig. S7.** Fig. 4d shows that MoON-2 has the largest  $C_{dl}$  of 527.2 mF cm<sup>-2</sup>, which is 4.5 times, 1.2 times, 1.1 times, 1.5 times, and 19.6 times larger than those of MoO<sub>2</sub> (117.2 mF cm<sup>-2</sup>), MoON-1 (443.0 mF cm<sup>-2</sup>), MoON-3 (482.2 mF cm<sup>-2</sup>), Mo<sub>2</sub>N (342.1 mF cm<sup>-2</sup>), and CC (26.9 mF cm<sup>-2</sup>), respectively. The larger ECSA of MoON series electrocatalysts is the result of the heterostructure between the MoO<sub>2</sub> and Mo<sub>2</sub>N phases for better activation of the surface sites. A larger  $C_{dl}$  implies more electrochemically active site exposure and accelerated HER. The electrocatalytic activity based on the ECSA is analyzed and shown in Fig. 4e. The intrinsic electrocatalytic activity of the MoON series electrocatalysts is superior to those of the pure phases of MoO<sub>2</sub>/CC and Mo<sub>2</sub>N/CC regardless of the ECSA because the interactions between the Mo-O and Mo-N species at the heterointerface promote the HER activity intrinsically. All in all, MoON-2 shows the best HER efficiency, demonstrating that a precisely modulated Mo-O/Mo-N configuration at the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface optimizes hydrogen adsorption in HER.

The turnover frequency (TOF) stands as a crucial benchmark for assessing the intrinsic activity of HER electrocatalysts. It is defined as the rate of conversion per active site in HER within a unit of time, ultimately determining the intrinsic activity of the electrocatalysts. The utilization of TOF effectively eliminates the comparability issues in catalytic activity stemming from varying catalyst loadings [40–42]. Therefore, TOF is studied to evaluate the intrinsic electrocatalytic capability of the Mo-based electrocatalysts (Supporting note). MoON-2 shows a bigger TOF of 0.20 s<sup>-1</sup> at an overpotential of 272 mV than the other electrocatalysts, confirming the excellent intrinsic electrocatalytic activity (Fig. 4f). The atomic interaction at the heterointerface would be

beneficial to the modified electronic structure of the active sites and optimized hydrogen adsorption properties, as a result enhancing the intrinsic catalytic capability of the active sites [30–32]. Fig. 4g illustrates the comparison of the overpotentials required for the current density of 1 A cm<sup>-2</sup> with those of previously reported electrocatalysts including Co-N-C (343 mV) [43], Nb<sub>1.35</sub>S<sub>2</sub> (370 mV) [44], Co/Se-MoS<sub>2</sub>-NF (382 mV) [45], MoSGMoS-0.3 (378 mV) [46], FeCoPd (400 mV) [47], Ni@NCW (401 mV) [48], HC-MoS<sub>2</sub>/Mo<sub>2</sub>C (412 mV) [49], MoS<sub>2</sub>/CNF (450 mV) [50], NP-MoS<sub>2</sub>/CC (480 mV) [51], MoSe<sub>2</sub>-Mo<sub>2</sub>N/Mo (485 mV) [52], N-MoO<sub>2</sub>/Ni<sub>3</sub>S<sub>2</sub> (517 mV) [53], Pd<sub>4</sub>S/Pd<sub>3</sub>P<sub>0.95</sub> (538 mV) [54], PtNb-Nb<sub>2</sub>O<sub>5</sub> (570 mV) [55], Pt-W<sub>18</sub>O<sub>49</sub> (743 mV) [56], 1.1 wt% Pt SAs/MoO<sub>2</sub> (800 mV) [57], Co-Co<sub>2</sub>P @ NPC/rGO (900 mV) [58], Rh/Si (950 mV) [59]. The results indicate that MoON-2 delivers excellent performance in large current density HER.

Fig. 5a shows the high durability of the MoON-2 electrocatalyst at a current density of 1 A cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 180 hours and the LSV curves of MoON-2 before and after the durability test are nearly the same (Fig. 5b). In addition, the morphology of MoON-2 is intact with nanowire array structure (Fig. S8), indicating the stable geometrical structure of the as-prepared electrocatalyst during the large current density HER. Fig. S9 shows similar diffraction patterns from the MoON-2 electrocatalyst before and after the long-time test. The XPS spectra of the electrocatalyst after the long-term test in Fig. S10 show similar spectra compared to the pristine sample with a concentration of Mo<sup>4+</sup>-O and Mo-N species of 44% and 35%, respectively, confirming the excellent stability of the surface chemistry of the electrocatalyst. The hydrogen production rate and Faradaic Efficiency (FE) of the MoON-2



**Fig. 5.** (a) Stability test of MoON-2; (b) LSV curves of MoON-2 before and after the stability test; (c) Experimental and theoretical amounts of H<sub>2</sub> and O<sub>2</sub> produced by MoON-2 and counter electrode, and FE at a current of 100 mA.

electrocatalyst are determined by the water displacement method schematically illustrated in Fig. S11. 53.0 mL of hydrogen and 26.5 mL of oxygen are produced by HER and OER, respectively for 70 min at a constant current of 100 mA. The high-purity H<sub>2</sub> is released from the acidic solution at a rate of  $1.86 \text{ mmol h}^{-1}$  (Fig. 5c) and FE is calculated to be as high as 99.8%.

### 3.3. DFT calculations

DFT calculations are conducted to elucidate the catalytic mechanism of the as-prepared electrocatalysts. MoO<sub>2</sub> (200) (Fig. S12a) and Mo<sub>2</sub>N (200) (Fig. S12b) are adopted to construct the heterointerface between MoO<sub>2</sub> and Mo<sub>2</sub>N phases (Fig. S12c) according to the XRD, TEM and HR-TEM results. At the pure MoO<sub>2</sub> (200) surface, the length of the Mo-O bond is in the range of 1.89 ~ 2.05 Å (Fig. S13a) and at the pure Mo<sub>2</sub>N (200) surface, the Mo-N bond length is 2.15 ~ 2.23 Å, as shown in Fig. S13b. In the MoO<sub>2</sub>(200)/Mo<sub>2</sub>N(200) heterostructure, the bond lengths of the Mo-O bond (2.12 ~ 2.16 Å) and Mo-N bond (2.26 Å) are longer than the Mo-O and Mo-N bond lengths, as shown in Fig. S13c. The results reveal that the changes in the bond length of Mo-O and Mo-N in the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface modulate the electronic structure of Mo sites at the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface, demonstrating the interactions between MoO<sub>2</sub> and Mo<sub>2</sub>N.

Generally, a  $\Delta G_{\text{H}^*}$  close to 0 eV is preferred for HER [60]. Hydrogen can adsorb on the Mo site of the pure phase of MoO<sub>2</sub> (H-MoO<sub>2</sub>) and Mo<sub>2</sub>N (H-Mo<sub>2</sub>N) as well as the Mo site of Mo<sub>2</sub>N phase (H-Mo(Mo<sub>2</sub>N)) and MoO<sub>2</sub> phase (H-Mo(MoO<sub>2</sub>)) at the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface, as indicated in Fig. 6a-d and S14. Fig. 6e reveals that the  $|\Delta G_{\text{H}^*}|$  value of the H-Mo(Mo<sub>2</sub>N) site at the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface is only 0.041 eV, which is closer to zero than that of H-Mo(MoO<sub>2</sub>) site of 0.080 eV, suggesting that the Mo(Mo<sub>2</sub>N) sites at the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface are the active centers in HER. Moreover, the  $|\Delta G_{\text{H}^*}|$  values of both the H-Mo(Mo<sub>2</sub>N) site and H-Mo(MoO<sub>2</sub>) site are smaller than those of the pure H-Mo<sub>2</sub>N (0.115 eV) and pure H-MoO<sub>2</sub> (0.207 eV), implying that the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface reduces the Mo-H binding and accelerates the release of hydrogen for faster kinetics. The band structure of the electrocatalysts in Fig. S15 indicates that the pure MoO<sub>2</sub>,

Mo<sub>2</sub>N, and MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface have a metallic nature. These results indicate that hydrogen adsorption capability on the Mo-based electrocatalysts can be optimized by modulating the Mo-O/Mo-N configuration at the MoO<sub>2</sub>/Mo<sub>2</sub>N heterointerface.

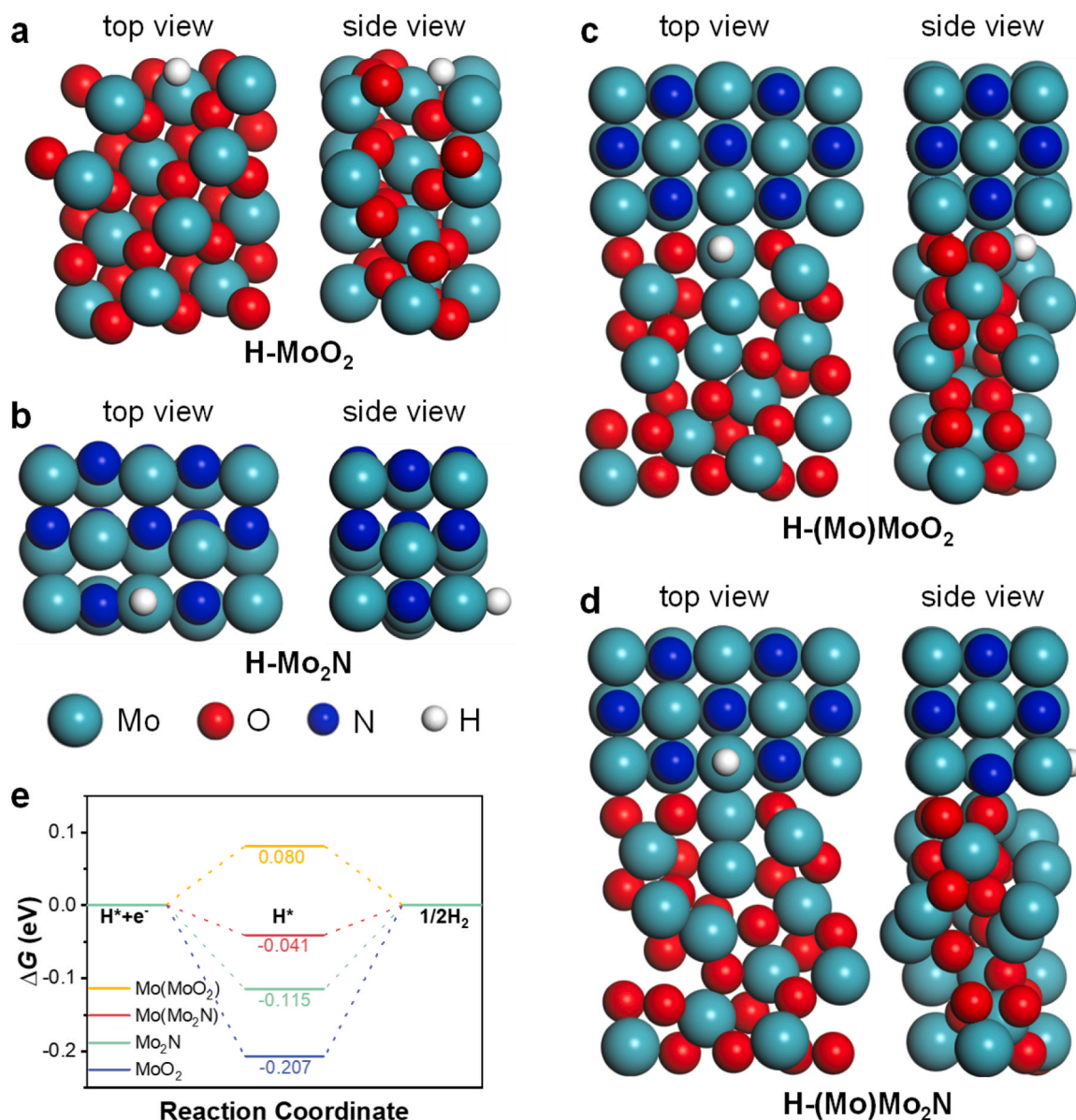
## 4. Conclusions

Heterostructured MoO<sub>2</sub>/Mo<sub>2</sub>N electrocatalysts with tunable Mo-O/Mo-N configurations are synthesized by a programmed nitridation process in ammonia with MoO<sub>3</sub> as the precursor. By precisely controlling the Mo-O and Mo-N contents in the heterostructure, the optimized Mo-O/Mo-N configuration shows weakened hydrogen adsorption characteristics as well as promoted HER kinetics. The MoO<sub>2</sub>/Mo<sub>2</sub>N electrocatalyst requires an overpotential of only 335 mV for an industrial-scale current density of  $1 \text{ A cm}^{-2}$  together with a Tafel slope of  $88 \text{ mV dec}^{-1}$  in 0.5 M H<sub>2</sub>SO<sub>4</sub>. In addition, the electrocatalyst exhibits excellent stability for 180 hours at a current density of  $1 \text{ A cm}^{-2}$  with an impressive Faradaic efficiency of 99.8% in HER. The MoO<sub>2</sub>/Mo<sub>2</sub>N heterostructure with the optimized Mo-O/Mo-N configuration has enormous potential in industrial applications. The results also provide valuable insights into the design and precise modulation of the electronic configurations of low-cost transition metal-based electrocatalysts for industrial-scale hydrogen production.

### CRedit authorship contribution statement

**Shuai Feng:** Methodology, Investigation, Roles/Writing – original draft, Visualization. **Donglian Li:** Methodology, Investigation, Roles/Writing – original draft, Visualization. **Hao Dong:** Investigation, Data curation, Visualization. **Song Xie:** Investigation, Formal analysis, Visualization. **Yaping Miao:** Software, Visualization. **Xuming Zhang:** Methodology, Funding acquisition, Visualization. **Biao Gao:** Methodology, Visualization. **Paul K. Chu:** Funding acquisition, Writing – review & editing, Visualization. **Xiang Peng:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing, Visualization, Project administration.





**Fig. 6.** Optimized surface structures of (a)  $\text{H-MoO}_2$ , (b)  $\text{H-Mo}_2\text{N}$ , (c)  $\text{H-Mo(MoO}_2\text{)}$ , and (d)  $\text{H-Mo(Mo}_2\text{N)}$ ; (e) Gibbs free energy diagram of  $\text{MoO}_2$ ,  $\text{Mo}_2\text{N}$ , and  $\text{MoO}_2/\text{Mo}_2\text{N}$ .

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123451](https://doi.org/10.1016/j.apcatb.2023.123451).

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